Improved ferroelectric performance of La:$Hf_{0.5}Zr_{0.5}O_2$ thin films

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Ferroelectricity (FE) in doped HfO_2 thin films firstly reported in 2011 [1] is now a quite relevant topic due to the possibility of its implementation into ferroelectric memory (FeRAM) since it provides many advantages over perovskites, including CMOS and BEOL compatibility. Moreover, HfO_2-based films may be successfully grown by ALD, which allows the possibility of 3D FeRAM realization and, therefore, solves its scaling challenge.

According to the general point of view, FE effect in HfO_2 is usually associated with the stabilization of the non-centrosymmetric polar o-phase *($Pca2_1$)*, confirmed both theoretically and experimentally [2,3]. Moreover, it has been already found that many dopants can provoke FE in HfO_2. However, different fundamental and technological tasks are upcoming. The most prominent $Hf_xZr_{1-x}O_y$ system demonstrates the clear FE response in wide stoichiometry range after annealing at relatively low T (≈400°C) [4]. However, its properties are usually much deteriorated by presence of parasitic non-FE m-phase. The most effective way to suppress m-phase stabilization was doping by La, Y and Gd [5-7]. However, its FE performance strongly depends on dopant concentration; moreover, a high-T annealing (≈550°C), exceeding the BEOL limit (400-450°C), was required.

Secondly, HfO_2-based FE films are characterized by high coercive field (1.0-1.5 MV/cm) compared to PZT (0.1-0.2 MV/cm) [8], which requires 2.5-3.0 V of operating voltage to achieve the saturated polarization value. Such field is very close to the breakdown one, which usually results in early hard breakdown. Practical switching endurance of such films is limited by value $\sim 10^9$, significantly smaller than for PZT ($\sim 10^{12}$). So, coercive field decrease is highly desirable.

The most recent work [9] described the possibility to combine advantages of low-level La doping with low crystallization temperature of HZO, which resulted in several interesting results. A significant decrease of the coercive field (by ~30%) was observed, which allowed applying lover voltage for ferroelectric switching and resulted in a great endurance improvement (up to 4×10^{10} cycles) while maintaining rather high $2P_r$ value. However, an unexpected transition from AFE-like material after 400°C annealing to clear FE after 450°C annealing was also observed.

Thus, the aim of the present work was a deeper insights into phase transitions in ternary La:$Hf_{0.5}Zr_{0.5}O_2$ system. For such task four different La concentrations in the range 0.7-2.1 mol. % were utilized. It was shown that the crystallization temperature of these films did not exceed 400°C. The detailed structural and electrical measurements were carried out to investigate such films. XRD data analysis allowed to expect t→o phase transition during La concentration variation, which was confirmed by small-signal CV measurements and DC-IV measurements which revealed a significant change in *k* value and leakage current density, respectively. In addition AFE-like to FE-like transition occurred during field cycling for two intermediate La concentrations. As a result of such detailed analysis rather promising ferroelectric response and long endurance following 5×10^{10} cycles with no breakdown was obtained.

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